



# Aqueous phase reforming of glycerol for hydrogen production over Pt–Re supported on carbon

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## ABSTRACT

Hydrogen production from the aqueous phase reforming of glycerol over 3%Pt–Re/C (1 and 3% Re) has been studied in the absence and presence of base, and the results compared with a Re-free 3%Pt/C catalyst. Although the Pt/C catalyst is very selective toward the production of hydrogen, catalytic activity is low. Addition of Re significantly increases the conversion of glycerol, at some loss of hydrogen selectivity to light hydrocarbons and water-soluble oxygenates. Addition of 1%KOH to the feedstock results in a small increase in glycerol conversion with 3%Pt–3%Re/C, an increase in the gas phase product selectivity in terms of H<sub>2</sub>/CO<sub>2</sub> ratio, and an increase in production of aqueous phase oxygenates. A modest increase in hydrogen gas phase selectivity with base addition with 3%Pt–3%Re/C arises primarily from reducing the selectivity toward C<sub>2</sub><sup>+</sup> alkanes, products that consume H<sub>2</sub>. In comparison, KOH addition to the glycerol feed with the Re-free 3%Pt/C catalyst provides an increase in glycerol conversion but results in a decline in both H<sub>2</sub> and alkane selectivity relative to aqueous phase oxygenates. The highest hydrogen productivity among the catalysts tested is achieved with a 3%Pt–3%Re/C catalyst with added KOH base. The observed product distributions can be understood in terms of the different reaction pathways that become emphasized depending on catalyst composition and pH.

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## 1. Introduction

Aqueous phase reforming for the production of hydrogen is an enabling technology with feedstocks such as sugars, sugar alcohols, and other polyols that are unstable at the operating temperature of conventional steam reforming [1]. Initial work from the Dumesic group pointed to the ability of supported platinum catalysts to produce hydrogen with good selectivity, although selectivity decreased as the number of carbons in the feedstock increased [2]. A substantial body of subsequent work by a number of different groups has focused on modifications to the catalyst to increase the activity to commercially acceptable rates, while retaining hydrogen selectivity. A variety of catalyst formulations based on both precious metal and non-precious metals have been described [3–12], but precious metal catalysts, most notably those including Pt, have shown the best performance [11,13]. Alloying of Pt with Ni or Co has also been described [14]. Addition of Re to the Pt metal improves catalyst activity significantly [15]. Due to issues of long-term hydrothermal stability, only a handful of supports can

be used in APR, with carbon being a leading support candidate and the support used in this investigation [8].

In this work, we have focused on the aqueous phase reforming of glycerol, and have compared a Pt/C catalyst with Pt–Re/C catalysts having the same Pt loading and different Re loadings. Gas phase glycerol reforming with similar catalysts has been reported [15–17], as well as glycerol APR with Pt/Al<sub>2</sub>O<sub>3</sub> catalyst [18,19]. More detailed studies of Pt–Re interactions will be provided in a subsequent publication. The goal of this work is increased hydrogen productivity, but the quantity and distribution of other products is also of interest. The selection of glycerol feedstock is based in part on its ready and cheap availability as a by-product of bio-diesel production, but more specifically it acts as a “model” polyol compound that undergoes the same types of reactions experienced by sugar alcohols such as sorbitol and xylitol, but with a simpler product slate. This facilitates the analysis, especially of the water-soluble oxygenated products. We have carried out our reactions at a relatively high space velocity. The purpose for this was to accentuate production of intermediate products, facilitating an uncovering of the different accessible reaction pathways, and an understanding of how they are affected by catalyst composition or reaction conditions. Operation at lower space velocities provides higher hydrogen selectivity.

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**Table 1**Catalyst total and metal surface areas and calculated metal dispersion by CO and H<sub>2</sub> chemisorption.

Catalyst	Pt (wt%) <sup>a</sup>	Re (wt%) <sup>a</sup>	CO uptake (μmol/g)	H uptake (μmol/g)	H/CO	Metal dispersion (%) <sup>b</sup>
3%Pt/C	3	0	116.2	147.4	1.27	75.6
3%Pt1%Re/C	3	1	69.5			45.2
3%Pt3%Re/C	3	3	67.1	116.5	1.74	43.6
3%Re/C	0	3	0.9	0.8		N/A

<sup>a</sup> wt% – g metal/100 g carbon.<sup>b</sup> Based on CO chemisorption.

Since reaction pathways leading to the formation of products such as mono-alcohols and alkanes could be the result of acid-catalysis, we have also examined the effect of base (KOH) addition to the feed on catalyst selectivity, in an effort to control the reaction pathways available to intermediates. We will show that addition of base, although it does successfully suppress some of the undesirable acid-catalyzed reactions in favor of those producing hydrogen, also facilitates undesirable reactions and therefore control of base concentration is necessary.

## 2. Experimental

### 2.1. Catalyst preparation

The catalysts were prepared using incipient wetness impregnation, using tetra-amine platinum dinitrate (Pt(NH<sub>3</sub>)<sub>4</sub>(NO<sub>3</sub>)<sub>2</sub>) and perrhenic acid (HReO<sub>4</sub>) as the platinum and rhenium sources, respectively. A high surface area activated carbon support (Engelhard, SSA 540 m<sup>2</sup>/g, pore volume 0.42 ml/g) was selected for this work. Specifically, for synthesis of the 3 wt%Pt/C catalyst (3%Pt/C), 20 g of the dried carbon support was impregnated with a solution prepared by dissolving 1.24 g of Pt(NH<sub>3</sub>)<sub>4</sub>(NO<sub>3</sub>)<sub>2</sub> into 8.4 g of DI water in a 30 ml glass vial, with shaking for at least 2 h prior to use. The impregnated sample was dried at 110 °C in air for 2 h and then calcined at 260 °C in air for 2 h with a ramp rate of 5 °C/min. A 3%Re/C catalyst was prepared analogously. For preparation of 3%Pt–Re/C catalysts, sequential impregnation was used. Specifically for preparation of 3%Pt–3%Re/C, 10 g of calcined 3%Pt/C catalyst was impregnated with 4.42 g of 7 wt% perrhenic acid solution, dried at 110 °C in air for 2 h, and calcined at 260 °C in air for 2 h.

Multi-point BET measurements were obtained with an Autosorb-6 gas sorption system (Quantachrome Corporation), after the samples were degassed overnight at 110 °C. CO and H<sub>2</sub> chemisorption were carried out at 45 °C using an Autochem II pulse chemisorption analyzer (Micromeritics). Prior to the chemisorption measurement, about 100 mg catalyst was first reduced in situ at 280 °C for 1 h in pure H<sub>2</sub> at a flow rate of 50 ml/min, then purged with He (for CO chemisorption) or Ar (for H<sub>2</sub> chemisorption) at 300 °C for 30 min at a flow rate of 50 ml/min, and finally cooled to 45 °C. The CO and H<sub>2</sub> chemisorption data are summarized in Table 1.

### 2.2. Catalyst testing

Experiments were carried out in a single channel microreactor with active heat exchange within the catalyst bed. This reactor has been described previously [20], and was used so that the activity measurements could be made under nearly isothermal conditions. A schematic of the experimental setup is provided in Fig. 1. The microchannel reactor body was made from SS316, and was enclosed by an oil-heating jacket with the oil being circulated using a Julabo oil pump. The reaction temperature was controlled within ±1 °C. The total effective volume of the reactor channel is about 0.45 ml (0.635 mm × 12.7 mm × 55 mm). A charge of 200 mg of cat-

alyst (60–100 mesh size) was packed into the narrow slot of the microchannel reactor, and a stainless steel screen (–325 mesh) and a stainless steel foam disk were placed on each side of the reactor to maintain the catalyst particles in place during experiments.

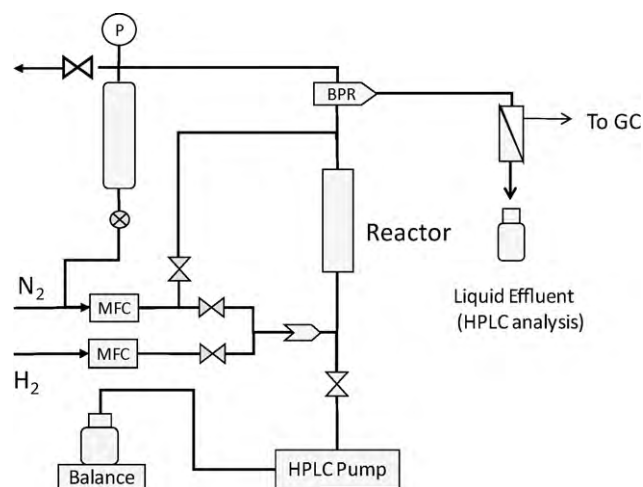
Prior to the reaction test, the catalyst was reduced at 280 °C for 2 h in 10 sccm of pure H<sub>2</sub> at atmospheric pressure. After purging the system with N<sub>2</sub> and cooling down to 60 °C, the backpressure regulator was set at the desired pressure (typically 425 psig), the aqueous feed solution comprising 10% glycerol (by weight) was introduced using a HPLC digital pump (Series III) at the desired feed rate, and heating of the catalyst bed was initiated. When the reactor reached the desired reaction temperature, in most cases 225 °C, N<sub>2</sub> flow was set at 10 sccm (N<sub>2</sub> served as an internal analytical standard). The system was allowed to stabilize for about 2 h prior to analysis of the reaction products. Gas product analysis was carried out using a micro gas chromatograph (Agilent Micro GC 3000C), equipped with two molsieve 5A columns, one Plot Q column, and one OV-1 column.

The liquid products were collected and analyzed with a Waters high performance liquid chromatograph (HPLC), comprising a HPLC pump, autosampler, and a refractive index detector. A Bio-Rad Aminex HPX-87H ion exclusion column (300 mm × 7.8 mm) was used for analyte separation. A 0.005 M H<sub>2</sub>SO<sub>4</sub> aqueous solution was used as eluent for this analysis at a flow rate of 0.55 ml/min. The data sets were processed and checked for carbon balance, which was typically >95%.

The glycerol conversion was determined by:

$$\text{Conversion (\%)} = 100 \times \text{moles glycerol reacted} / \text{moles glycerol fed}$$

The selectivity to H<sub>2</sub> is defined as the ratio of the amount of H<sub>2</sub> produced divided by the amount of H<sub>2</sub> that could be produced if all the converted glycerol had undergone complete reforming to produce H<sub>2</sub> and CO, and all CO shifted to CO<sub>2</sub>. Under this definition, one mole of converted glycerol could generate 7 mol of

**Fig. 1.** Microchannel reactor schematic.

**Table 2**

Gaseous products of aqueous phase reforming of 10% glycerol over Re–Pt/C catalysts at 225 °C, 420 psi, WHSV = 5/h.

Catalyst	Feed	Conversion (%)	H <sub>2</sub> productivity (l/lcat-h)	H <sub>2</sub> selectivity (%)	Gas phase selectivity (%)	H <sub>2</sub> /CO <sub>2</sub>	TOF (carbon based, min <sup>−1</sup> )			
							Glycerol	H <sub>2</sub>	CO <sub>2</sub>	Alkane
3%Pt/C	Glycerol	5.3	151	56.5	71.8	2.1	1.3	1.8	0.8	0.1
	Glycerol + KOH	41.5	299	14.4	20.8	1.9	10.2	3.5	1.9	0.3
3%Pt1%Re/C	Glycerol	52.4	842	30.8	53.1	1.3	26.0	10.9	8.1	2.8
	Glycerol + KOH	77.2	833	20.7	27.0	2.1	25.2	15.9	7.7	0.6
3%Pt3%Re/C	Glycerol	88.7	1154	24.5	58.5	1.4	34.7	23.3	16.1	4.8
	Glycerol + KOH	89.4	1245.8	26.1	34.3	2.0	35.0	25.1	12.7	1.2

Data were measured at 225 °C, 420 psig, WHSV = 5/h.

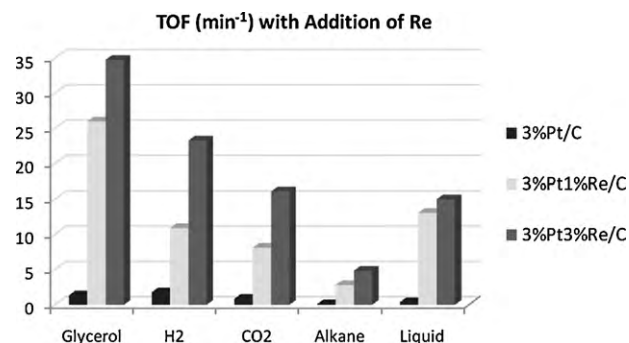
H<sub>2</sub> and 3 mol of CO<sub>2</sub>. The selectivity of the other carbon containing products refers to the percentage of carbon present in this product relative to the total carbon available based on converted glycerol.

### 3. Results and discussion

#### 3.1. Catalyst characterization

The BET surface area, measured for the Pt/C and Pt–Re/C catalysts, remained similar to that measured for the carbon support alone (about 540 m<sup>2</sup>/g). Table 1 summarizes the chemisorption results for the various Pt/C, Pt–Re/C, and Re/C catalysts used in this work. On the 3%Pt/C catalyst, the irreversible CO uptake indicates a metal dispersion of 75.6%, based on the assumption of a CO:M ratio of unity. On the other hand, the H<sub>2</sub> chemisorption suggests a dispersion value near unity (for H/M = 1). On Pt surfaces the tendency for bridge bonding to occur can lead to an underestimation of metal dispersion by CO chemisorption [21]. This may explain the discrepancy between the CO and H<sub>2</sub> results. Addition of Re to the Pt/C results in a decrease in both the CO and H<sub>2</sub> chemisorption values (Pt loading remaining constant), however the decrease in CO chemisorption is significantly greater than for H<sub>2</sub>. The CO and H<sub>2</sub> uptake values for 3%Re/C alone are very low. We note that the low CO chemisorption value with 3%Re/C, as well as the decrease in CO chemisorption values observed in our work following Re addition, differ from the results reported by Simonetti et al. [15] and Kunkes et al. [16]. In these latter studies, the temperature of reduction (450 °C) was substantially greater than used in our work (280 °C), which could well affect the degree of Re reduction, and its subsequent alloy formation with Pt. Moreover, differences in catalyst preparation (co-impregnation vs. sequential), Pt metal source (H<sub>2</sub>PtCl<sub>6</sub>·6H<sub>2</sub>O vs. Pt(NH<sub>3</sub>)<sub>4</sub>(NO<sub>3</sub>)<sub>2</sub>), type of carbon (carbon black vs. activated carbon), and temperature at which the chemisorption measurements were made (27 °C vs. 45 °C) may also contribute to the disparity in the results. The importance of pretreatment on Pt–Re/Al<sub>2</sub>O<sub>3</sub> has been emphasized [22].

The decrease in CO and H<sub>2</sub> chemisorption upon Re addition could be the result of several factors including (i) the Pt–Re particles are larger; (ii) Re (oxide) locates preferentially at the particle surface; (iii) Re alters the electronic structure of Pt, affecting its chemisorption properties and/or its reducibility. The fact that the H<sub>2</sub> chemisorption is less affected than the CO chemisorption following Re addition complicates the determination of Pt dispersion and the calculation of active sites as well as determination of turnover frequencies (TOFs). According to both the CO and H<sub>2</sub> chemisorption data, there appear to be fewer Pt surface sites available for catalysis following the addition of Re (assuming that only Pt is responsible for CO and H<sub>2</sub> chemisorption), which will have an effect of accentuating the calculated turnover frequencies for the Pt–Re/C catalysts relative to Pt/C.

**Fig. 2.** Effect of Re addition to 3%Pt/C on catalyst activity (turnover frequency, TOF).

#### 3.2. Effect of addition of rhenium to Pt/C on glycerol aqueous phase reforming

The gas phase product distributions and calculated turnover frequencies (based on CO chemisorption) for glycerol conversion and H<sub>2</sub>, CO<sub>2</sub>, and alkane production from the APR of glycerol at 225 °C and 420 psig for the Pt/C and Pt–Re/C catalysts are summarized in Table 2. For high glycerol conversions, the turnover frequencies are underestimated, assuming a non-zero order rate dependence on glycerol. The trend in performance with increasing Re loading is shown in Fig. 2, in terms of TOF. These results reflect initial catalyst performance, obtained after lineup of the reactor system (approximately 2 h). The Pt/C catalyst stands out in terms of having very high selectivity toward hydrogen (see Table 2), but displays very low glycerol conversion under these conditions. The addition of Re to 3%Pt/C has a dramatic effect in increasing the glycerol conversion, even though a catalyst comprising only Re (3%Re/C) is inactive for the APR of glycerol (data not shown).

As a trade-off for increasing glycerol conversion at a fixed space velocity, the high selectivity toward hydrogen decreases in favor of greater alkane selectivity when Re is added. It is notable that the carbon based selectivity to gas phase products (CO<sub>2</sub> + CO + alkanes) for the 3%Pt–Re/C catalysts are similar, in the range of 53–59%, distinctly lower than that of the 3%Pt/C catalyst. Thus, although glycerol conversion increases with increasing Re content, this is not accompanied by an increase in gas phase product selectivity at these space velocities. The effect of Re promotion on H<sub>2</sub> selectivity is shown in Fig. 3, where space velocity was adjusted in order to compare performance at comparable conversion level. It can be seen that, at comparable conversion, the Re promoted catalysts show lower H<sub>2</sub> selectivity. However, due to the greater glycerol conversion with addition of Re at fixed space velocity, all Re-containing catalysts show higher hydrogen productivity than 3%Pt/C (Table 2).

Table 3 quantifies the liquid phase product distribution produced from these same catalysts at the same space velocity. In order to more fairly compare the effect of Re promotion on catalyst selectivity, the 3%Pt/C catalyst performance is compared to

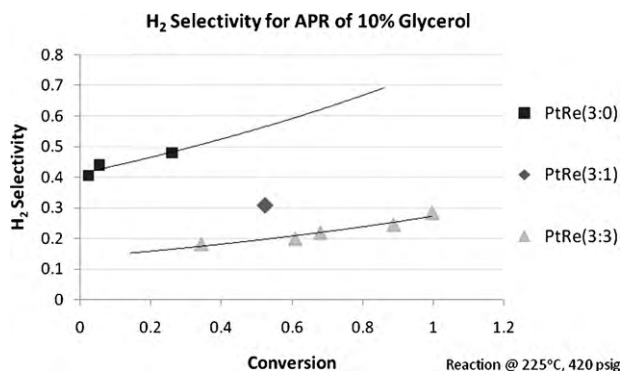


Fig. 3. H<sub>2</sub> selectivity as function of conversion for catalysts with different Pt/Re ratios.

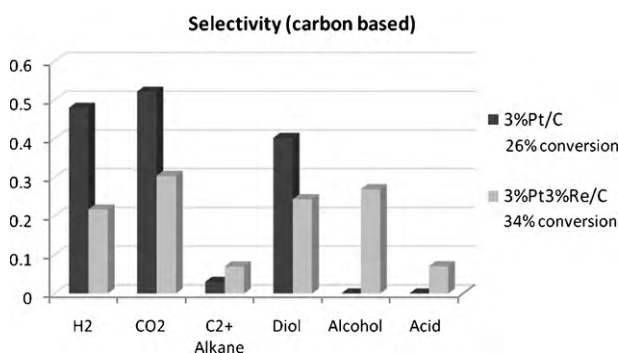


Fig. 4. Effect of Re addition to 3%Pt/C on product distribution.

3%Pt–3%Re/C at similar glycerol conversion in Fig. 4. We were unable to distinguish chromatographically between acetone and isopropanol, and several mass spectroscopic analyses of the liquid product established that both are present although acetone tends to predominate. For convenience, and since isopropanol is a reduction product of acetone, the acetone/isopropanol peak has been collectively lumped under “alcohol” in Fig. 4. With the Re-free 3%Pt/C, the liquid products are limited to ethylene glycol (EG) and propylene glycol (PG), with no evidence of monohydric alcohols or carboxylic acids even up to 26% conversion of glycerol. The addition of Re results in higher conversion, however, it also results in higher alkanes and liquid phase product selectivity. In addition, reaction pathways leading to alcohols and acids are facilitated as shown in Fig. 4.

The promotional effect of Re on Pt-based catalysts for aqueous phase reforming has not been definitively resolved. Re promotion of Pt-based catalysts for the water gas shift reaction has been reported in the literature. A Pt–Re/TiO<sub>2</sub> catalyst was shown to be more active than Pt/TiO<sub>2</sub> [23]. The role of Re in enhancing the activity was

attributed to the presence of ReOx species under the WGS reaction conditions. The ReOx species provide an additional redox pathway, in which ReOx is reduced by CO, generating CO<sub>2</sub>, and re-oxidized by H<sub>2</sub>O, forming H<sub>2</sub> [24]. On the other hand, Sato et al. attributed the increase in activity of Pt–Re/TiO<sub>2</sub> to Pt–Re bimetallic formation, which resulted in stronger CO adsorption [25]. An enhancement in activity of Pt/ZrO<sub>2</sub> by Mo and Re promotion was reported by Ruettinger et al. [26]. The Pt–Re, Pt–Mo and Pt–Re–Mo alloy formation was shown to be responsible for the enhanced activity. For gas phase glycerol reforming, Kunkes et al. attributed the increase in activity by Re addition to weakened CO adsorption [16]. The conflicting arguments on whether Re addition to Pt results in stronger or weaker CO adsorption could possibly be attributed to a particle size effect. Ruettinger et al. reported that CO adsorption is weaker on small Pt–Re particles and stronger on the larger Pt–Re particles [26]. Since part of the Re is present as ReOx under the hydrothermal reaction conditions of glycerol APR (detailed evidence for this will be provided in a separate publication), we believe that Re may have a dual effect on Pt:

- Pt–Re alloy formation leads to an increased rate of dehydrogenation and decarbonylation.
- ReOx (acidic) species promote dehydration pathways leading to liquid products (propylene glycol, acids and alcohols) and alkanes.

More details on Pt–Re alloy formation and its effect on the electronic structure of Pt is under investigation and will also be the subject of a future publication. The effect of ReOx acidity on the reaction pathway is discussed in more detail below.

### 3.3. Reaction pathways

A plausible reaction pathway for the desired production of hydrogen from glycerol is shown in the box at the top of Fig. 5. The initial step involves dehydrogenation to form an aldehyde (glyceraldehyde) intermediate, which subsequently de-carbonylates (C–C bond scission) to produce CO and a C<sub>2</sub>-diol moiety. This dehydrogenation–decarbonylation sequence is repeated until complete conversion of glycerol to CO and H<sub>2</sub> is obtained. The mechanism by which the carbon–carbon bond cleavage occurs is subject to some debate. Carbon–carbon bond cleavage catalyzed by adjacent metal (Pt) sites [19], as well as the retro-aldol reaction of glyceraldehyde, both offer plausible pathways, although the latter is more facilitated at higher pH [27]. In the presence of base, Maris and Davis have argued that C–C bond breakage over Pt is primarily via a base-catalyzed pathway rather than through metal-centered catalysis, whereas with Ru the C–C bond cleavage is metal catalyzed [28]. Wawrzet et al. have asserted that a combination of metal and acid-based reactions over a bifunctional catalyst must be invoked to explain their experimental results for glycerol APR [19].

Table 3

Aqueous phase product distribution from aqueous phase reforming of 10% glycerol over Pt/C and Pt–Re/C catalysts at 225 °C, 420 psi, WHSV = 5 h<sup>−1</sup>.

Catalyst	Feed	Conversion (%)	Liquid selectivity (carbon based, %)	Selectivity to liquid products (carbon based, %)						
				EG	PG	1-Propanol	2-Propanol <sup>a</sup>	EtOH	MeOH	Acid
3%Pt/C	Glycerol	5.3	26.9	6.2	20.7					
	Glycerol + KOH	41.5	77.4	7.2	52.5	0.5	0.7	6.7	0.0	9.7
3%Pt1%Re/C	Glycerol	52.4	41.7	6.0	13.7	5.0	6.8	7.1	0.7	2.5
	Glycerol + KOH	77.2	67.3	7.8	37.2	1.1	1.3	8.9	1.1	10.2
3%Pt3%Re/C	Glycerol	88.7	36.8	1.3	4.2	4.7	14.3	5.5	0.5	5.6
	Glycerol + KOH	89.4	54.2	3.0	23.2	2.5	1.4	8.9	1.0	11.8

Data were measured at 225 °C, 420 psig, WHSV = 5 g Gly/gcat-h.

<sup>a</sup> Including 2-propanol and acetone.



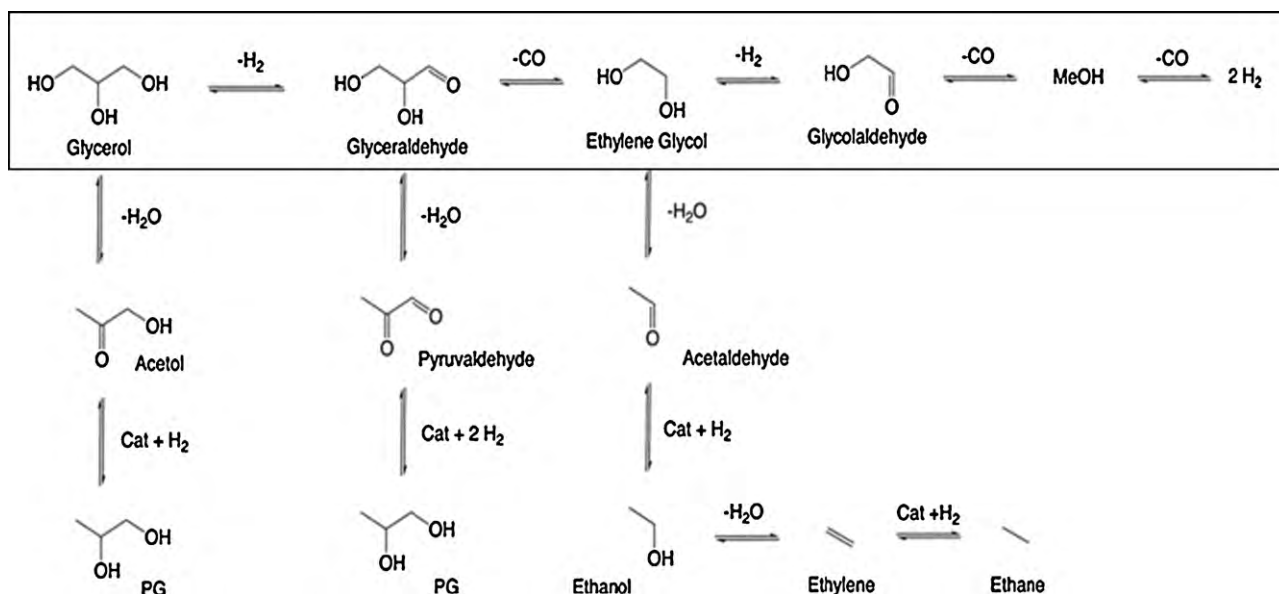


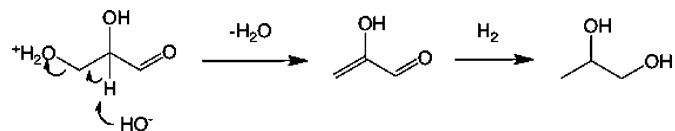
Fig. 5. Possible reaction pathways in APR of glycerol over Pt/C and Pt-Re/C catalysts.

Alternate reaction pathways are required to explain the appearance of the other liquid phase and gas phase products, and a plausible series of representative pathways (excluding carboxylic acid production) is also provided in Fig. 5. These are primarily routes through C–O bond cleavage or scission, which compete with the desired dehydrogenation–decarbonylation pathway. For the C–O scission pathway, the net effect is consumption of one mole of  $H_2$  per C–O bond broken. The  $CO_2$  produced reflects the selectivity for C–C cleavage through the preferred pathway shown in the box in Fig. 5. A plausible method to express the relative importance of  $H_2$  generating (C–C cleavage) vs.  $H_2$  consuming (C–O cleavage) pathways is through the use of the relative  $H_2$  yield (RHY). RHY is defined as the ratio: (measured  $H_2/CO_2$ )/(theoretical  $H_2/CO_2$ ). Thus, as the C–O cleavage pathway becomes more pronounced, the RHY becomes <1 and drops progressively.

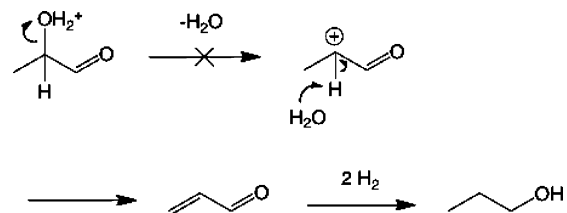
In the case of 3%Pt/C, the detected liquid phase products were limited to EG and PG, as mentioned earlier. Therefore, on Pt/C, the only  $H_2$  consuming reaction pathway is the conversion of glycerol to PG. The RHY for Pt/C with glycerol under the conditions tested was 0.9. PG could be formed either via dehydration of initially formed glyceraldehyde to pyruvaldehyde followed by addition of two moles of hydrogen, or direct dehydration of glycerol through an acetol intermediate followed by subsequent hydrogenation [29,30]. The dehydration–hydrogenation pathway through acetol has been proposed to occur under acidic environments as a route to propylene glycol over Ru/C [31,32], copper chromite [33], Cu–ZnO [34], and recently with Pt/ $Al_2O_3$  and Pt black [19], wherein it was asserted that Pt black generates the necessary acidity to proceed through an acetol intermediate. Since the aqueous medium in our experiment was mildly acidic, and 3%Pt/C exhibited some acidity by  $NH_3$  TPD (data not shown), it was inferred that PG could be generated via a dehydration–hydrogenation pathway through such an acetol intermediate. This would suggest that the more acidic ReOx could favor this pathway to convert glycerol. We note, however, that our test with 3%Re/C showed no activity, suggesting that although acetol might be a dehydration-based intermediate, subsequent conversion to observable products such as PG requires a metal hydrogenation function that is not provided by Re or ReOx alone.

The alternate pathway of dehydration of initially formed glyceraldehyde to pyruvaldehyde is facile and, for reasons described below, the more likely pathway for PG formation over 3%Pt/C.

Glyceraldehyde is more active towards dehydration chemistry compared to PG and EG because it can proceed through a bimolecular elimination reaction shown below. The combination of the terminal OH leaving group and acidity of the alpha-hydrogen to the aldehyde allows glyceraldehyde to dehydrate readily in the presence of a weak acid. In contrast the aldehydes of PG and EG do not have a leaving group on the terminal carbon and therefore would proceed through a unimolecular elimination reaction (also shown below). Unimolecular elimination reactions require either a strong leaving group or strong acid catalyst, neither of which are present during glycerol APR over Pt/C. This is evidence by the fact that there was no observed dehydration of PG or EG to form other liquid products on Pt/C.



Dehydration of glyceraldehyde by an elimination bimolecular E2 pathway.



Dehydration of PG by an elimination unimolecular E1c pathway.

When Re is added to Pt/C, the TOF of glycerol and products increases, as is shown in Fig. 2. Re addition results in lower selectivity to hydrogen relative to alkanes, and the overall gas phase product selectivity decreases as shown in Fig. 4. The major selectivity change in the aqueous phase products as a result of the addition of Re to Pt/C is the significant increase in alcohol products and  $C_2^+$  alkanes, along with the appearance of carboxylic acids, all at the expense of diol products. The reason for this change in selectivity with Re may be the result of ReOx species on the surface generating acidity [35], facilitating the dehydration–hydrogenation pathways at the expense of initial dehydrogenation to glyceraldehyde

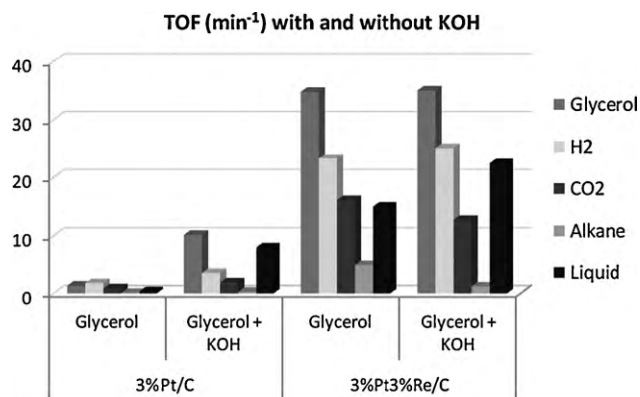


Fig. 6. Effect of KOH addition on activity (TOF) over Pt/C and Pt–Re/C.

which would be followed by carbon–carbon bond cleavage (decarbonylation). Analogously, formation of alcohols could occur by dehydration–hydrogenation of diols (propanols from PG, ethanol from EG), and formation of ethane and propane analogously via dehydration–hydrogenation of alcohols. Since separate experiments (not shown) showed no methanation or Fischer–Tropsch activity with Pt–Re, methane formation is likely due to reforming (decomposition) of ethanol. As mentioned above, the dehydration of alcohols and diols is less favored due to the EI chemistry required for dehydration. This explains the low selectivity of Pt/C for alkanes. In the case of Pt–Re/C, the enhanced acidity of ReOx results in higher selectivity to alkanes, albeit still low relative to CO<sub>2</sub>. On Pt/C, the PG/EG ratio increases with conversion, suggesting a much lower activity of PG relative to EG. In contrast, on Pt–Re/C the PG/EG ratio was almost independent of conversion (data not shown) which consistent with the additional reaction pathways facilitated by ReOx, as discussed above.

The formation of carboxylic acids is less readily explained, but a combination of hydration/dehydrogenation reactions of aldehydic intermediates through a redox mechanism on ReOx provides a possible pathway. By retarding the dehydration pathways, higher H<sub>2</sub> yields might be achieved since dehydration–hydrogenation consumes H<sub>2</sub>. For this reason we decided to investigate the effect of base addition to the feed, to provide a higher pH medium with the intention to inhibit undesirable acid-catalyzed dehydration reactions.

### 3.4. Effect of base addition on APR of glycerol

#### 3.4.1. 3%Pt/C + KOH

The above-described APR experiment with glycerol over 3%Pt/C was repeated with addition of KOH at 1000 ppm concentration (initial pH ~12). The catalyst activity with and without KOH at the same space velocity is shown in Fig. 6. The increase in TOF for glycerol conversion is dramatic with addition of base, but this primarily reflects the production of a greater amount of liquid products, not hydrogen. Despite a nearly eightfold increase in the TOF for glycerol conversion, the hydrogen TOF is increased by about a factor of two. The sharp increase in activity with addition of KOH could be ascribed to modification of Pt by K. The promotional effect of K<sup>+</sup> has been extensively reported. Recently, Tanaka et al. studied modification of Pt with alkali for preferential CO oxidation, and pointed out that the addition of K<sup>+</sup> makes Pt more electron deficient, reducing the interaction between CO and Pt [36]. However, that modification of Pt by K<sup>+</sup> was achieved by K<sup>+</sup> addition to the catalyst prior to reaction, and the reaction medium was gas phase. In our experiments, the surface modification occurred by interaction of solution phase K<sup>+</sup>OH<sup>−</sup> with the solid catalyst. Therefore, we

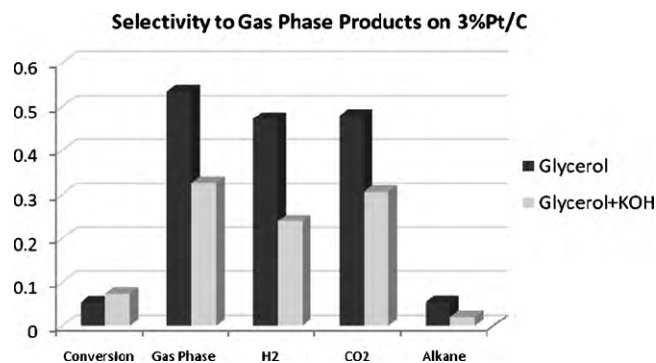


Fig. 7. Effect of KOH addition on gas phase product distribution over 3%Pt/C.

cannot discount the possible contribution of OH<sup>−</sup> adsorption on the surface.

In addition to activity enhancement, the presence of KOH also changed the reaction pathway over 3%Pt/C. The gas phase and liquid phase product selectivities at similar conversions are provided in Figs. 7 and 8. It can be seen that H<sub>2</sub> and CO<sub>2</sub> selectivity both decreased with addition of KOH. The H<sub>2</sub>/CO<sub>2</sub> ratio, indicative of competition between C–C and C–O scission, decreased from 2.09 to 1.84 on addition of base. This suggests C–C bond cleavage is less favored relative to C–O bond cleavage. C–O bond cleavage could be enhanced by base-catalyzed dehydration of glyceraldehyde, but is less probable with glycerol because the C–H protons are not sufficiently acidic to be abstracted by base. We believe this chemistry is similar to that described by Feng et al. who showed that with a Ru/TiO<sub>2</sub> catalyst PG formation arises from base-catalyzed dehydration of glyceraldehyde to form the alpha-hydroxy enal followed by subsequent hydrogenation [37]. EG and PG, like glycerol, are unable to undergo base-catalyzed dehydration, which may explain the higher selectivity to EG and PG with added base. This is consistent with the results of Maris and Davis [28]. Another effect of KOH is possibly to assist the Cannizzaro reaction, facilitating the production of lactic acid, which was not observed with 3%Pt/C in the absence of base. The production of paired lactic acid and PG through the Cannizzaro reaction could also contribute to the observed increase in PG.

#### 3.4.2. 3%Pt–Re/C + KOH

When operating under alkaline pH, increasing the Re loading from 0 to 1% and then to 3% resulted in a progressive increase in conversion. Gas phase product selectivity decreases in all cases with the addition of base, whereas a modest increase in hydrogen selectivity and productivity is seen only with 3%Pt–3%Re/C, as shown in Table 2. The 3%Pt–3%Re/C catalyst with added 1%KOH provided the greatest hydrogen productivity of all the catalysts tested in this

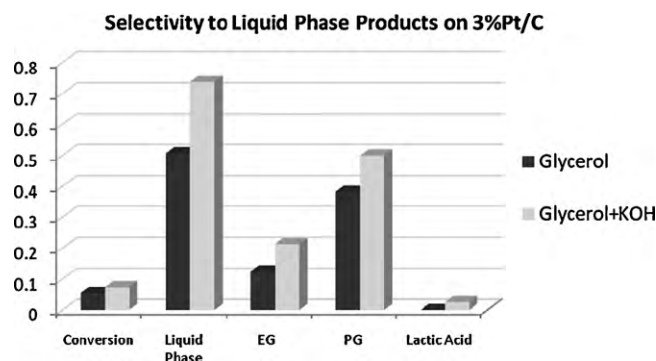


Fig. 8. Effect of KOH addition on liquid phase product distribution over 3%Pt/C.

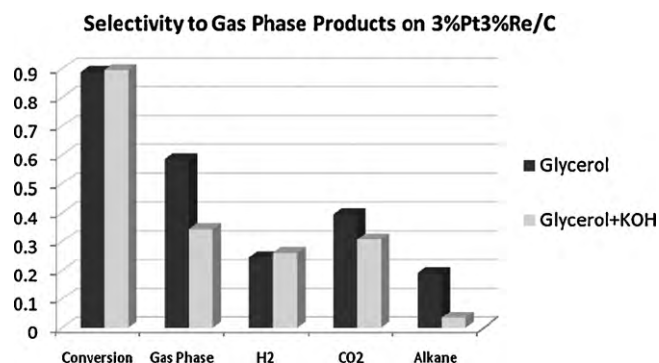


Fig. 9. Effect of KOH addition on gas phase product distribution over 3%Pt–3%Re/C.

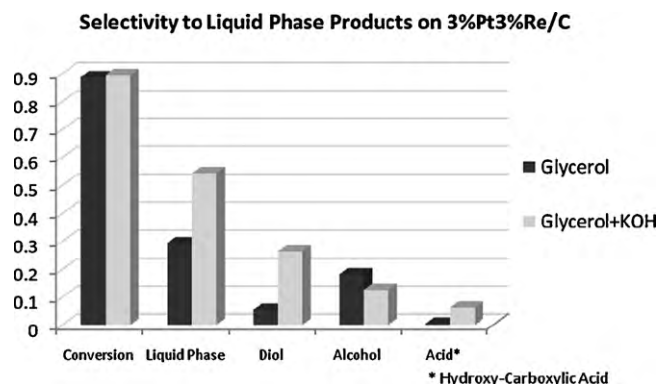


Fig. 10. Effect of KOH addition on liquid phase product distribution over 3%Pt–3%Re/C.

study, primarily the result of higher conversion rather than a significant improvement in H<sub>2</sub> selectivity. The liquid products resulting from addition of KOH are summarized in Table 3. Especially notable is the substantial increase in PG and PG/EG ratio of the 3%Pt–Re/C catalysts when base is added, as was the case with 3%Pt/C. We believe that this is due to a facilitated pathway involving facile base-catalyzed dehydration of initially formed glyceraldehyde to pyruvaldehyde, followed by hydrogenation to PG. Base-catalyzed dehydration of PG is difficult, as described above, explaining its higher concentration in the product.

A direct comparison of the selectivities of the best performing catalyst, 3%Pt–3%Re/C, with and without KOH present, is provided in Figs. 9 and 10. For the gas phase products, addition of KOH decreased CO<sub>2</sub> selectivity by 25% while H<sub>2</sub> selectivity was increased slightly. The higher H<sub>2</sub>/CO<sub>2</sub> (Table 2) with addition of base implies less consumption of H<sub>2</sub> by the C–O bond cleavage pathway. This implies that the dehydration pathways (facilitated by ReOx) to form alcohols and alkanes is suppressed, which is consistent with the observed lower selectivity to alcohols and alkanes and higher selectivity to diols. This trend suggests that the addition of base operates to a significant extent to neutralize the acidity provided by the ReOx component to the catalyst. The higher hydrogen productivity of 3%Pt–3%Re/C when KOH is added is most specifically seen to be a result of the pathway to gas phase alkane production becoming disfavored. If we examine this at one more level of detail, we see that the fraction of methane of the total alkanes [ $C_1/(C_1 + C_2 + C_3)$ ] is 0.31 for the base-free case and 0.69 when KOH is present. Thus, base addition to the 3%Pt–3%Re/C catalyst is especially effective in reducing the production of C<sub>2</sub><sup>+</sup> hydrocarbons, presumably by dis-favoring the dehydration–hydrogenation of alcohols. Again, the greater selectivity of diols and corresponding carboxylic acids could also be attributed, in part, to the base-catalyzed Cannizzaro reaction.

## 4. Conclusions

In the APR of glycerol, a 3%Pt/C catalyst shows good selectivity toward H<sub>2</sub> but has relatively low activity. Addition of Re increases the activity of the catalyst and overall hydrogen productivity, although it is accompanied by a decrease in H<sub>2</sub> selectivity. The addition of Re to Pt/C increases the rate of carbon–carbon bond cleavage, as shown by the significantly higher glycerol conversion and hydrogen productivity that results. Two key steps, both believed to be metal catalyzed, are required for hydrogen production: dehydrogenation of the polyol to form an aldehydic intermediate (glyceraldehyde), and carbon–carbon bond cleavage of glyceraldehyde to generate CO and H<sub>2</sub> and ethylene glycol. Additional H<sub>2</sub> is produced by the water gas shift of the formed CO. Production of other products, for example propylene glycol (PG), appears to be due to competitive reactions involving dehydration and subsequent hydrogenation reactions. The dehydration step is likely acid-catalyzed. Although the source of this acidity with Pt/C is not obvious, it could derive from acid sites on the carbon support or on the metal itself. With the Pt–Re/C catalyst, it appears likely that some ReOx is present on the catalyst surface and it can provide acidity to facilitate dehydration pathways. At lower space velocities (higher glycerol conversion), more H<sub>2</sub> and less liquid product are produced with 3%Pt–3%Re/C, suggesting that by providing greater residence time the dehydrogenation–carbon cleavage pathway can compete more favorably with the dehydration-based route.

Base was added to these catalysts in an effort to decrease the acid-catalyzed dehydration pathways (the result of ReOx acidity) leading to oxygenated products. For 3%Pt/C, base addition increased conversion to liquid phase oxygenated products, most notably to PG and to a lesser extent EG, but did not significantly increase H<sub>2</sub> production. Addition of base to 3%Pt–3%Re/C resulted in a small increase in H<sub>2</sub> selectivity and a decrease in C<sub>2</sub><sup>+</sup> alkane selectivity. Base addition increased the fraction of liquid products, with an increase in PG being especially pronounced. The 3%Pt–3%Re/C catalyst is sufficiently active that base-catalyzed transformations that increase oxygenates appear to have somewhat less of an effect compared with 3%Pt/C. It appears that the catalyst performance is mediated significantly by the Pt–Re interaction. The higher hydrogen productivity with KOH addition over 3%Pt–3%Re/C (compared to the KOH-free case) appears to be primarily the result of a decrease in the production of C<sub>2</sub><sup>+</sup> alkanes. Further studies aimed at gaining a better understanding of the role of basicity and its optimization to maximize benefit for the APR chemistry is the subject of ongoing work.

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